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Heat Capacity and Thermal Expansion of Water and Helium

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Original expressions for heat capacity CV and its components, vibrational and configurational components of thermal expansion coefficient were established. The values of CV, Cvib, Cconf, αvib and αconf for water and helium 4He were calculated.

Keywords: heat capacity, thermal expansion coefficient, isothermal compressibility, vibrational input, configurational input, water, helium 4.

Introduction

The heat capacity at constant volume ($C_V = dU/dT$) according to the definition of internal energy ($U = U_{Kin} + U_{Pot}$) has two components. In expression [1] C_V and α_P components associated with various types of motion of the molecules and their component parts (vibrations, librations, translations, etc.) are called «vibrational» (C_{vib}, α_{vib}) , and the components associated with molecular configuration changes – «configurational» (C_{conf}, α_{conf}):

$$C_V = C_{vib} + C_{conf} \quad (1)$$

$$\alpha_p = \alpha_{vib} + \alpha_{conf} \quad (2)$$

Phenomenological thermodynamics relates heat capacity at constant pressure C_P and constant volume C_V by ratio

$$C_P - C_V = \frac{T\alpha_p^2 V_0}{\gamma_T} \quad (3)$$

where V_0 – molar volume, T – temperature (K), $\alpha_p = (1/V)\cdot(\partial V/\partial T)_P$ – isobaric thermal expansion coefficient, $\gamma_T = -(1/V)\cdot(\partial V/\partial P)_T$ – isothermal compressibility factor, ($C_{Therm} = T\alpha_P^2 V_0/\gamma_T$) – heat capacity caused by thermal expansion.

Activation of mechanical degrees of freedom taking place in the substance under the given conditions (including molecule translations) increases the volume, so «vibrational» thermal expansion coefficient should be positive ($\alpha_{vib} > 0$).

Expression (3) with (2):

$$C_P - C_V = \frac{T\alpha_{vib}^2 V_0}{\gamma_T} + \frac{T\alpha_{conf}^2 V_0}{\gamma_T} + \frac{2T\alpha_{vib}\alpha_{conf} V_0}{\gamma_T} \quad (4)$$

In order to determine the type of heat capacity components we consider the following:

- α_{vib} and α_{conf} should have opposite signs, as there are states of matter (water, helium, ...) in which $\alpha_p = 0$;
- expression for C_p and C_V should include α_{vib} and α_{conf};
- component ($T\alpha_{vib}^2 V_0/\gamma_T$) should go to the expression for C_{vib} (increase in oscillation amplitude leads to increase in the kinetic component of internal energy) and $C_{therm} = T\alpha_P^2 V_0/\gamma_T$ (thermal expansion of the system volume is observed);
- expression for C_V should include negative sign, as value $C_V > 0$, and α_{vib}, α_{conf} have different signs.

Given these conditions and expressions (1) - (4) we get:

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$$C_P = \frac{T\alpha_{vib}^2 V_0}{\gamma_T} + \frac{T\alpha_{conf}^2 V_0}{\gamma_T} \quad (5)$$

$$C_V = -2TV_0\alpha_{vib}\,\alpha_{conf}/\gamma_T \quad (6)$$

$$C_{conf} = \frac{T\alpha_{conf}^2 V_0}{\gamma_T} \quad (7)$$

$$C_{vib} = \frac{T\alpha_{vib}^2 V_0}{\gamma_T} + \frac{T\alpha_p^2 V_0}{\gamma_T} \quad (8)$$

Replacing α_{conf} with (α_p − α_{vib}) in (5) we obtain a quadratic equation the physical meaning of which has the following solution:

$$\alpha_{vib} = \frac{\left\{\alpha_p + \left[\frac{2C_P\gamma_T}{TV_0} - \alpha_p^2\right]^{1/2}\right\}}{2} \quad (9)$$

Expressions (1) – (9) allow us to find value C_V, C_{vib}, C_{conf}, α_{vib} and α_{conf}, if we know values V_0, C_P, γ_T and α_p.

Calculated values α_{vib}, α_{conf}, C_{conf} and C_{vib} for water H_2O and liquid helium ^4He are shown in Tables (1-5) and Figs. (1-4). For this research, condensed state of water and helium are interesting because dependence $V_0 = f(T)$ and dependence $\alpha_p = f(T)$ of these substances have extreme points.

Water

Reference values C_P, C_V, V_0, α_p , γ_T [3-5] and calculated values α_{conf}, C_V, C_{vib}, C_{conf} and C_{Therm} for protium water from 273.15 to 373.15 K are shown in Tables 1 and 2.

From Tables 1 and 2 we can see that the vibrational and configurational components of thermal expansion

Table 1 V_0, C_P, γ_T and α of water at atmospheric pressure [3-5]

T, K	V_0, 10^{-6} m^3/ mol	C_P, J/ mol·K	γ_T, 10^{-11} Pa^{-1}	α, 10^{-4} K^{-1}		
				α_P	α_{vib}	α_{conf}
273.15	18.0184	76.028	50.886	-0.681	19.482	-20.163
277.13	**18.0165**	**75.850**	**49.514**	**0.000**	**19.393**	**-19.393**
283.15	18.0214	75.595	47.811	0.879	19.253	-18.374
293.15	18.0484	75.397	45.895	2.066	19.087	-17.021
303.15	18.0948	75.307	44.774	3.031	18.981	-15.950
313.15	18.1574	75.289	44.243	3.890	18.949	-15.059
323.15	18.2341	75.307	44.260	4.514	18.922	-14.408
333.15	18.3236	75.361	44.500	5.290	19.006	-13.716
343.15	18.4254	75.451	45.210	5.830	19.078	-13.248
353.15	18.5388	75.595	46.160	6.472	19.237	-12.765
363.15	18.6634	75.757	47.310	6.990	19.375	-12.385
372.85	18.8010	75.950	50.404	7.532	19.857	-12.325
373.15	18.7990	75.973	48.900	7.537	19.599	-12.062

Table 2 Heat capacity of water and its components at atmospheric pressure

T, K	C, J/ mol·K				
	C_V, ref	C_V, calc	C_{vib}	C_{conf}	$(TV_0\,\alpha_P^2)/\gamma_T$
273.15	76.028	75.983	36.664	39.320	0.045
277.13	-	**75.850**	**37.925**	**37.925**	**0.000**
283.15	75.433	75.513	39.480	36.033	0.082
293.15	74.820	74.905	41.506	33.399	0.492
303.15	74.226	74.181	43.014	31.168	1.126
313.15	73.469	73.344	44.201	29.144	1.945
323.15	72.640	72.594	44.956	27.638	2.713
333.15	71.740	71.522	45.715	25.808	3.839
343.15	70.320	70.698	46.151	24.547	4.753
353.15	69.848	69.654	46.544	23.110	5.941
363.15	68.875	68.757	46.781	21.976	7.000
372.78	-	68.062	46.939	21.123	7.888
373.15	67.884	67.825	46.954	20.871	8.149

have opposite signs; dependence $\alpha_{vib} = f(T)$ has a minimum value in a temperature range of (30−50)°C approximately where the value of heat capacity C_P is minimal It follows from Table 1 that the increase in thermal expansion coefficient of water in the range of ($T_{melt} - T_b$) is caused by a decrease in modulus α_{conf}.

According to Morgan and Warren [6], melting ice and heating water from 0 to 62°C simultaneously increase the number of nearest neighbors of the molecule and the average intermolecular distance. Decrease in the volume of condensed water during melting and heating from 0°C to 3.98°C is explained by the fact module α_{conf} in these processes is greater than α_{vib} [2] (volume reduction due to increase in the number of nearest neighbors molecule is greater than increase in volume because of the growth of intermolecular distance). At a temperature of maximum density (3.98°C) water $|\alpha_{conf}| = \alpha_{vib}$. With further heating, the volume of water increases as $\alpha_{vib} > |\alpha_{conf}|$.

Reference value α_p and calculated values α_{vib} , α_{conf} in liquid water at saturation line from 373.15 K to subcritical $T \geq 0.96\ T_c$ (T_c – critical temperature) are shown in Table 3. Type of dependences $\alpha_{vib} = f(T)$ and $\alpha_{conf} = f(T)$ are shown in Fig. 1. The values α_P and γ_T were determined using $\left(\frac{\partial V}{\partial T}\right)_P$, $\left(\frac{\partial V}{\partial P}\right)_T$ [3-5].

Table 3 Reference α_P and calculated values C_{vib}, C_{conf}, α_{vib} and α_{conf} at saturation line in liquid water

T, (K)	C_{vib}, J/ mol·K	C_{conf}, J/ mol·K	α_P, 10^{-4} K^{-1}	α_{vib}, 10^{-4} K^{-1}	α_{conf}, 10^{-4} K^{-1}
373.15	46.954	20.871	7.537	19.599	-12.062
393.15	47.257	20.403	7.900	19.904	-12.004
403.15	47.314	19.085	8.650	20.346	-11.696
413.15	47.286	17.964	9.350	20.806	-11.456
423.15	47.397	17.529	9.750	21.194	-11.444
433.15	47.391	16.751	10.400	21.772	-11.372
443.15	47.595	16.540	10.800	22.304	-11.504
453.03	47.047	14.810	12.151	23.315	-11.164
485.52	46.755	12.740	14.876	26.019	-11.143
506.99	**46.864**	**11.587**	**17.266**	**28.609**	**-11.343**
523.48	46.704	10.613	19.645	31.199	-11.554
537.07	46.683	9.888	22.089	33.961	-11.872
548.71	46.796	9.279	24.720	36.947	-12.227
558.95	46.795	8.683	27.603	40.180	-12.577
567.95	46.734	8.086	30.848	43.756	-12.908
576.46	46.908	7.604	34.492	47.839	-13.347
584.11	47.356	7.194	38.689	52.550	-13.861
591.19	47.663	6.769	43.529	57.938	-14.409
597.79	48.084	6.358	49.320	64.351	-15.031
603.96	48.779	5.989	56.355	72.130	-15.775
609.78	49.619	5.634	65.200	81.903	-16.703
615.27	51.427	5.490	77.200	95.654	-18.454
617.90	51.112	5.079	84.900	103.634	-18.734
620.47	53.193	5.177	93.000	113.055	-20.055
622.97	53.086	4.723	**104.100**	**124.435**	**-20.335**
625.41	53.758	4.507	115.900	137.114	-21.214
627.79	60.559	5.284	129.900	154.735	-24.835
630.11	58.086	4.309	152.300	176.704	-24.404
632.37	57.464	3.708	180.500	205.401	-24.901
634.59	58.027	3.251	220.000	246.115	-26.115
638.86	55.811	1.963	377.000	404.491	-27.491

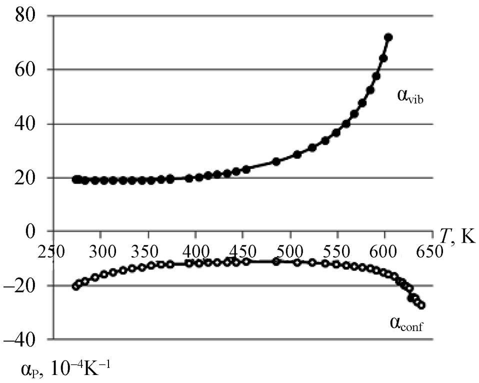

Fig. 1 Temperature dependence of Calculated values α_{vib} and α_{conf} of water at saturation line

Helium

For calculation of values α_{vib}, α_{conf}, C_{conf} and C_{vib} for liquid helium ^{4}He we use C_P, C_V V_0, α and γ_T (Tables 4−6) [7-9]. Thermal expansion coefficient according to [7, 8] in the temperature range of (1.15−1.20) K (Fig. 2) and in the temperature range of (2.15−2.20) K is equal to zero. It allows us to define vibrational and configurational inputs to the thermal expansion coefficient of liquid ^{4}He.

Liquid ^{4}He can exist in two fractions: He II and He I. Helium II – a fraction with a superfluid component (superfluid), the proportion of which varies from 1 for 0 K to 0 for T_λ=2.1768 K (the temperature of λ- transition) [8].

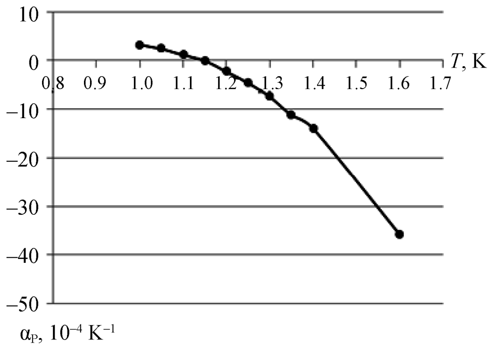

Fig. 2 Temperature dependence of thermal expansion coefficient

Tables 4 and 5 provide reference and calculated values of liquid ^{4}He II at atmospheric pressure.

The values of heat capacities C_P and C_V, C_V and α_P components of liquid helium at saturation line are given in Table 6. Fig. 3 shows the dependence $\alpha_{conf} = f(T)$ and Fig. 4 - dependence of configurational and vibrational heat capacity of liquid helium at saturation line.

Results and discussion

The separation of heat capacity C_V and thermal expansion coefficient α_P into components is good for studying the mechanism of formation of thermal and structural properties of the liquid state. For example, Tables 1−3 show that value α_{conf} decreases for water being heated from melting temperature (T_{melt}) to T_{max}≈0.785T_c≈508 K.

Table 4 V_0, α_P,γ_T, C_P, and C_V of liquid ^{4}He II at atmospheric pressure [8]

T, K	V_0, 10^{-6} m^3/mol	α_P,10^{-4} K^{-1}	γ_T, 10^{-8} Pa^{-1}	C_P, J/ mol·K	C_V, J/ mol·K
0.6	27.580	1.749	12.147	0.017733	0.017729
0.8	27.582	3.213	12.156	0.084307	0.084286
1.0	27.583	3.294	12.193	0.42047	0.42043
1.05	27.584	2.495	12.210	0.58638	0.58638
1.10	27.584	1.225	12.225	0.79320	0.79316
1.15	27.584	0.04805	12.249	1.04364	1.04364
1.20	27.584	-2.215	12.264	1.34183	1.34179
1.25	27.584	-4.523	12.290	1.68626	1.68622
1.30	27.583	-7.342	12.313	2.10721	2.10705
1.35	27.582	-11.17	12.335	2.63215	2.63179
1.4	27.580	-13.87	12.374	3.23962	3.23902
1.6	27.566	-35.79	12.492	6.21083	6.20643
1.8	27.539	-65.82	12.641	11.73602	11.71881
1.9	27.516	-87.32	12.720	15.48686	15.45564
2.0	27.488	-112.8	12.943	20.82753	20.77349
2.05	27.471	-141.6	13.169	23.70460	23.61894
2.10	27.449	-177.0	13.267	26.72456	26.58847

Table 5 Vibrational and configurational inputs to C_V and α_P of liquid ^{4}He II

T, K	α_{vib}, 10^{-4} K^{-1}	α_{conf}, 10^{-4} K^{-1}	C_{vib}, J/ mol·K	C_{conf}, J/ mol·K
0.6	81.545	-79.796	0.009054	0.008674
0.8	153.987	-150.774	0.043023	0.041265
1.0	154.014	-150.720	0.053651	0.051389
1.15	448.907	-448.859	0.52188	0.52176
1.20	497.466	-499.685	0.66788	0.67390
1.40	713.519	-727.389	1.58803	1.65099
1.60	919.775	-955.565	2.98241	3.22391
1.80	1189.93	-1255.75	5.53515	6.18366
2.00	1508.38	-1621.18	9.6100	11.1635
2.10	1662.96	-1839.96	11.87926	14.70921

Table 6 Characteristics of liquid ^{4}He at saturation line [9]

T, K	Heat capacity, J/ mol·K					α_P, 10^{-4} K^{-1}	
	C_P, ref	C_V, ref	C_{vib}	C_{conf}	C_V, calc	α_{vib}	α_{conf}
0.800	0.089738	0.089698	0.04604	0.04366	0.08970	159.593	-155.348
0.900	0.19877	0.19873	0.1010	0.0977	0.19874	222.524	-218.746
1.000	0.40106	0.40106	0.2018	0.1993	0.40105	298.081	-296.233
1.050	0.55706	0.55706	0.2756	0.2751	0.55076	340.084	-339.704
1.100	0.74128	0.74128	0.3693	0.3720	0.74128	384.757	-386.153
1.150	0.97944	0.97944	0.4858	0.4936	0.97941	431.860	-435.321
1.200	1.27123	1.27123	0.6279	0.6432	1.27114	481.131	-486.922
1.400	3.12083	3.12003	1.52108	1.59881	3.11989	697.426	-714.805
1.600	6.41617	6.41216	3.09664	3.31590	6.41254	939.191	-971.303
1.800	11.75964	11.74763	5.61745	6.13142	11.74888	1207.600	-1260.428
2.000	20.761	20.721	9.690	11.030	20.720	1541.129	-1640.729
2.100	28.995	28.883	13.1126	15.7704	28.8830	1786.887	-1951.315
2.150	37.100	36.844	16.1210	20.7235	36.8445	1990.535	-2239.186
2.200	16.899	16.855	9.015	7.840	16.855	1472.226	-1369.590
2.400	9.506	9.014	5.772	3.240	9.012	1181.181	-849.306
2.600	9.286	8.337	5.739	2.599	8.338	1214.368	-757.060
2.800	9.618	8.125	5.889	2.233	8.122	1286.177	-707.248
3.000	10.395	8.249	6.215	2.034	8.249	1382.066	-681.733
3.200	11.592	8.686	6.728	1.958	8.686	1505.551	- 678.676
3.400	12.940	9.134	7.248	1.888	9.136	1652.886	-683.180
3.600	14.413	9.510	7.717	1.791	9.508	1826.996	-688.107
3.800	16.078	9.802	8.133	1.665	9.798	2043.173	-694.489
4.000	18.088	10.022	8.507	1.515	10.022	2325.440	-703.190
4.200	20.693	10.199	8.855	1.334	10.199	2716.396	-715.920
4.400	24.404	10.343	9.197	1.152	10.349	3300.384	-734.475
4.600	30.380	10.479	9.548	0.933	10.481	4276.202	-760.995
4.800	42.067	10.627	9.966	0.685	10.651	6247.818	-804.068

In [10] it is shown that at T_{max} volume multiplied by pressure of saturated gas $(PV_0)_S$, and molecular packing coefficient (K_S) in liquid saturation line branch have the maxima. Further heating of water (Table 3) increases value α_{conf}. Value $\Delta\alpha_{conf}/\Delta T$ in the temperature range of (273.15−373.15) K and at T>0.96T_c is considerably higher than in other temperature ranges. This fact shows that at low (273.15−373.15) K and high (T> 0.96T_c) temperatures structural changes occur more intensely. In the dependence $\alpha_{conf} = f(T)$ two distinct temperatures (T_{max}≈ 0.785T_c and T≈0.96T_c) may be attributed to temperature of quasi-phase transition in liquids [11].

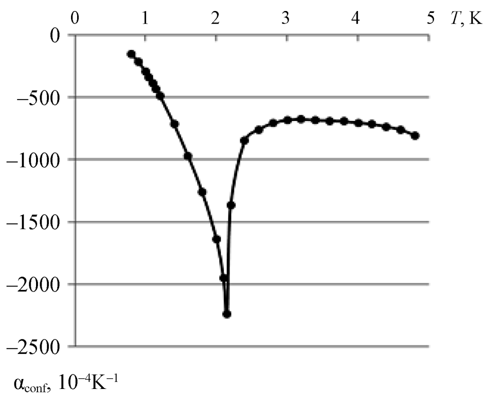

Fig. 3 $\alpha_{conf} = f(T)$ of liquid ^{4}He at saturation line

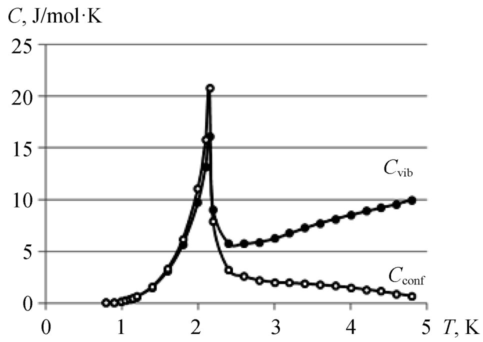

Fig. 4 $C_{vib} = f(T)$ and $C_{conf} = f(T)$ of liquid ^{4}He at saturation line

Analysis of dependence $C_{conf} = f(T)$ (Tables 2 and 3) shows that C_{conf} is constantly decreasing with the increase in temperature of water. Ratio C_{conf}/C_V for water according to our data is 0.518 (273.15 K) and 0.308 (373.15 K)), and according to [1] it is approximately equal to 0.50 (273.15 K) and 0.35 (373.15 K).

In [12,13] calculated are the values of radial distribution of water. It was found that by heating water under pressure 1000 bar from 298 K to 450−500 K the number of nearest neighbors of Z in water molecules increases from 4.9 to 5.7, and after further heating - it decreases to about 4.3 at 773 K. From Table 3 and Fig. 1 we see that the value of configurational components of thermal expansion coefficient is constantly decreasing from melting temperature to 506.99 K. 506.99 K is almost equal to T_{max} and is close to the upper limit of temperature range of (450-500) K.

Change of Z may be related to the change of α_{conf}. If the increase in Z is accompanied by the decrease of α_{conf}, the increase in modulus α_{conf} must be accompanied by the decrease of Z. At $T>T_{max}$ modulus α_{conf} in liquid water is constantly increasing, so we should expect decrease of Z for water molecules in the interval T_{max}–T_c. This assumption may be confirmed by temperature dependence K_S for water at saturation line [10]: K_S increases up to T_{max} and then decreases.

From Tables 5 and 6 we see that modulus α_{conf} for liquid ^{4}He increases from almost 0 K to $T = 4.8$ K (Table 6), except for the interval $T_\lambda \approx 3$ K. We could expect that in He II and He I in the temperature range 3-4.8 K the number of nearest neighbors of atoms will decrease (according to [14] the value of Z for ^{4}He atoms in the temperature range of 3-5.1 K decreases).

Low accuracy in determining the experimental characteristics of Helium (C_P, C_V, ρ, α_P, γ_T) does not allow us to unambiguously interpret the dependence $\alpha_{conf} = f(T)$ at high temperatures. For this reason, we used temperature 4.8 K as the maximum temperature of liquid ^{4}He.

In the temperature range (0 K - T_λ) vibrational C_{vib} and configurational C_{conf} components of heat capacity increase; in the temperature range (2.6–4.8) K C_{vib} increases and C_{conf} for the He I, as it happens to water at temperature from 273.15 K to 638.86 K, constantly decreases (Fig. 4).

In conclusion, the original expressions for heat capacity C_V and its components were proposed, and the separation of thermal characteristics of the substance to «vibrational» and «configurational» components is good for a better understanding of the structural changes in the liquid state was shown.

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